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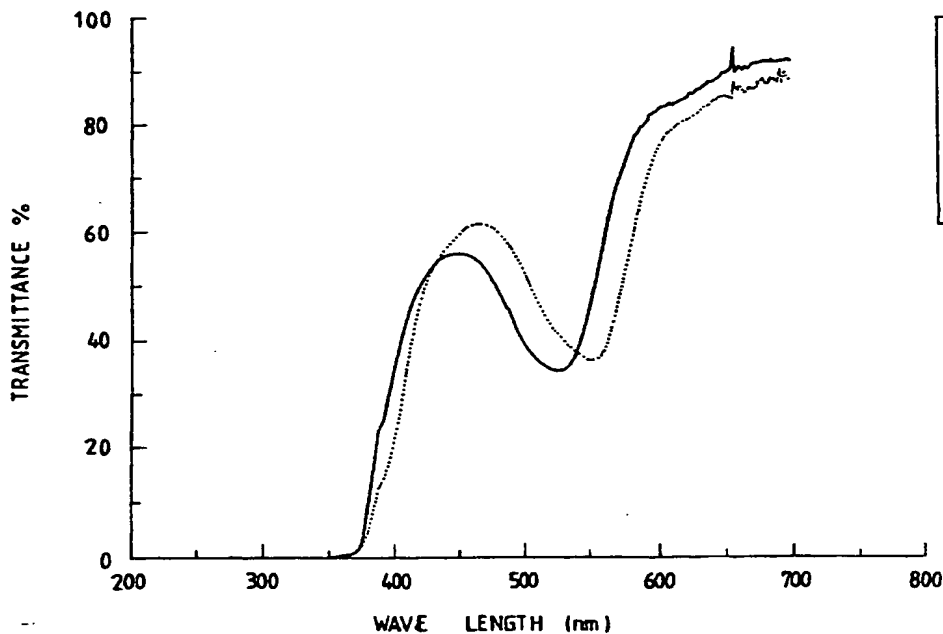
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(54) Title: LIQUID COMPOSITION POLYMERIZABLE INTO PHOTOCHROMATIC ORGANIC GLASS



(57) Abstract: Liquid composition polymerizable, by means of radicalic polymerization, into photochromatic organic glass, comprising a polymerizable allyl carbonate, a polymerization initiator capable of generating free radicals under the polymerization conditions and a photochromatic compound.

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LIQUID COMPOSITION POLYMERIZABLE INTO PHOTOCHROMATIC ORGANIC GLASS.

The present invention relates to a liquid composition polymerizable into photochromatic organic glass.

More specifically, the present invention relates to a liquid composition polymerizable, by means of radicalic polymerization, into photochromatic organic glass having good optical and physico-mechanical characteristics, comprising a polymerizable allyl carbonate, a polymerization initiator capable of generating free radicals under the polymerization conditions and a photochromatic compound.

A further object of the present invention relates to the photochromatic organic glass obtained by the polymerization of said composition and the end-products obtained starting from this composition such as, for example, ophthalmic and safety plates and lenses.

Photochromatic compounds are substances which have the characteristic of reversibly changing color and/or de-

gree of light transmission when exposed to certain types of electromagnetic radiation and solar light, returning to their original color and transmission state when the initial light source is removed.

5 There are numerous substances with photochromatic characteristics, which belong to various groups of both organic and inorganic compounds such as, for example, those described in the texts "Photochromism", by G.H. Brown (Ed.), Vol. III of the Weissberger series "Tech-
10 niques of Organic Chemistry", Wiley Interscience, New York (1971); "Photochromism: Molecules and Systems", by H. Dürr and H. Bouas-Laurent (Ed.), Vol. 40 of the series "Studies in Organic Chemistry" Elsevier (1990).

 Among organic photochromatic compounds, those belong-
15 ing to the groups of spiro-indoline-oxazines, spiro-pyrans and chromenes, are particularly known and used.

 The above compounds are capable of giving photochromatic characteristics to polymerized organic materials which can be used in the production of photochromatic ar-
20 ticles as described, for example, in the following patents: EP 315,224, EP 442,166, EP 432,841, EP 524,692, EP 245,020, U.S. 5,005,576, U.S. 5,110,922, U.S. 3,567,605 and U.S. 5,066,818.

 The above organic photochromatic compounds can also
25 be used in the field of organic glass, in particular when

said organic glass is used for the preparation of photochromatic optical articles.

Various polymers which can be used for the preparation of organic glass for the optical industry, are known in the art. Among these, for example, polyacrylates, polycarbonate, cellulose acetyl butyrate, polystyrene and polyurethanes, can be mentioned. Among the types of organic glass of considerable commercial importance, is that deriving from the polymerization of allyl carbonates of diols or polyols, as described, for example, by F. Stein in: "Encyclopedia of Chemical Processing and Design", I Ed. Dekker. Inc., New York (1964), page 452 onwards; or in European patent EP 35,304.

Numerous methods are known in literature, for introducing photochromatic organic compounds into materials generally defined as organic glass.

The methods described consist, for example, in introducing a suitable layer of material, containing the photochromatic substance, between two layers of organic glass. This method however is difficult and costly and, furthermore, as the end-products obtained consist of different materials joined by means of adhesives, they tend to lose their structural unity or, in any case, the good properties characteristic of organic glass.

Another method consists in the surface impregnation

of organic glass by immersing the glass in a solution of the photochromatic substance in an organic solvent using a technique similar to the color bath method ("dip-dyeing"). The drawbacks of this technique consist in the use of organic solvents which are often flammable, the very lengthy immersion times and the possibility of damaging the organic glass during the long contact with the solvent.

Alternatively, the photochromatic compound can be applied by means of thermal transfer as described, for example, in European patent EP 316,980, or by transfer in vapor phase. Also these methods, however, have various drawbacks: the photochromatic compound, in fact, remains localized in the surface layers of the end-product and is therefore subject to the degrading action of atmospheric agents.

Other methods consist in dispersing the photochromatic compound in paints or resins which are then deposited on the surface of the lens or organic glass in general.

These systems also have the disadvantages described above: complexity, high cost and often limited performances and, in addition, as it is known that the fatigue strength depends on the quantity of photochromatic compound used, end-products with a limited duration are obtained with the above methods.

It is known, on the other hand, that end-products obtained by the polymerization of a monomer widely used in the organic glass industry such as diethyleneglycol bis(allyl carbonate), known under the trade-name of
5 CR 39® of PPG Industries or RAV 7® of Great Lakes Chemical Corporation, in the presence of a photochromatic compound belonging to the group of spiro-indoline-oxazines or spiro-pyrans, do not have a photochromatic activity due to degradation of the active principle as a result of the
10 radicalic polymerization initiators normally used such as, for example, di-isopropyl percarbonate, dicyclohexyl percarbonate and dibenzoyl peroxide. This inconvenience, however, is not surprising for experts in the field, as it is known that almost all organic dyes used in the preparation
15 of colored organic glass, do not resist the drastic polymerization conditions to which the diethylene-glycol-bis(allyl carbonate) is subjected.

The first to overcome the disadvantages of the known art described above are Italian patent IT 1,255,878 and
20 European patent application EP 595,424.

Italian patent IT 1,255,878 describes the preparation of photochromatic organic glass with a high refractive index by means of the radicalic polymerization of a urethane resin of the acrylate and/or methacrylate and/or styrene
25 type. The photochromatic compounds belonging to the groups

of spiro-pyrans, spiro-oxazines and chromenes, are introduced into the monomeric mixture and do not seem to undergo significant degradation during the polymerization. However, even if the end-products thus obtained have good
5 photochromatic characteristics, this preparation has a drawback relating to the high increase in the production costs due to the resin used.

Numerous preparations based on acrylates and styrene matrixes containing photochromatic products in mass, have
10 been described in the last few years, but very few based on allyl carbonates.

A further great improvement with respect to the known art consists of European patent application EP 595,424 mentioned above, which describes a polymerizable liquid
15 composition which is also useful for the preparation, by means of mass polymerization, of photochromatic organic glass. This composition, consisting of a poly(allyl carbonate) of an aliphatic or cycloaliphatic polyol, must be polymerized using initiators of the peroxide type belonging
20 to the group of perketals.

The polymerizations carried out using the above composition and radicalic initiator, proceed without any substantial degradation of the photochromatic compound or organic dye introduced into the polymerizable mixture.

25 The use, however, of spiro-indolino-naphtho-oxazines

and spiro-indolino-quino-oxazines known in the art, having position 6 of the naphthalene or quinoline ring free, causes, after polymerization, a bright and persistent reddish-purple coloring in the organic glass which strongly reduces the initial transmittance of the organic glass and makes it aesthetically unacceptable.

This is due to the fact that, as described for example in "Journal of Organic Chemistry" (1995), Vol. 60, pages 5446-5448, when the above position 6 is free, the C=C double bond undergoes a radicalic addition to give stable adducts having a reddish-purple coloring.

As most spiro-indolino-naphtho-oxazines and spiro-indolino-quino-oxazines having a blue coloring in the activated state, have position 6 free, they give a bright coloring every time they are used in mass polymerization. This greatly limits the possibility of obtaining photochromatic organic glass based on polyallyl carbonate, having a neutral (gray or brown) coloring: this coloring is mainly requested in the field of ophthalmic lenses in which the photochromatic compounds or organic dyes are directly present in the polymerization mixture.

The Applicant has now surprisingly found that the use of particular compounds belonging to the group of spiro-isoindolino-oxazines do not give the above bright and persistent reddish-purple coloring.

This allows even blue photochromatic compounds to be used in a mixture with other products to obtain liquid compositions polymerizable into photochromatic organic glass having neutral shades.

5 An object of the present invention therefore relates to a liquid composition polymerizable, by means of radicalic polymerization, into photochromatic organic glass, comprising a polymerizable allyl carbonate, a polymerization initiator capable of generating free radicals
10 under the polymerization conditions and a photochromatic compound, characterized in that:

(A) said polymerizable allyl carbonate is at least a poly(allyl carbonate) of an aliphatic C_3-C_{10} polyol, linear or branched, or of a cycloaliphatic C_5-C_{12}
15 polyol, said polyols containing from 2 to 6 hydroxyl groups in the molecule, said poly(allyl carbonates) being in the form of monomers or mixtures of monomer and relative oligomers;

(B) said polymerization initiator, capable of generating
20 free radicals, is at least a compound selected from the group of perketals;

(C) said photochromatic compound is at least an organic photochromatic compound selected from the group of spiro-isoindolino-oxazines.

25 Component (A)

As indicated above, allyl carbonates useful for the purposes of the present invention are poly(allyl carbonates) of aliphatic polyols containing from 3 to 10 carbon atoms in the linear or branched chain. Poly(allyl carbonates) of cycloaliphatic polyols containing from 5 to 16 carbon atoms in the molecule can also be used for the purpose. These polyols may generally contain from 2 to 6 hydroxyl groups in the molecule, preferably from 2 to 4. Mixed poly(allyl carbonates) can also be used, i.e. deriving from two or more polyols, which can be obtained by the mechanical mixing of poly(allyl carbonates) of the single polyols, or directly by chemical reaction starting from diallyl carbonate and from a mixture of polyols, as specified hereunder in greater detail. Finally, all the above poly(allyl carbonates) can be in the form of a monomer, or a mixture of the monomer with the relative oligomers. The poly(allyl carbonates) (A) are generally products which are liquid at room temperature, with a viscosity ranging from 10 cst to 500 cst, measured at 25°C and their oligomer content can vary within a wide range, for example, from 0% to about 80% by weight.

In accordance with what is described above, examples of poly(allyl carbonates) (A) which can be used for the purposes of the present invention are:

25 - bis(allyl carbonates) of diols such as, for example,

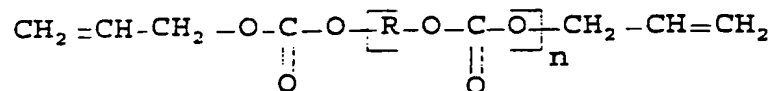
diethylene glycol, dipropylene glycol, triethylene glycol, tetraethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 3-methyl-1,5-pentanediol, 2-methyl-2-ethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol, 1,4-dimethylolcyclohexane, 4,8-bis(hydroxymethyl)[5.2.1.0^{2,6}]tricyclocane, etc.;

- tris(allyl carbonates) of triols such as, for example, glycerol, trimethylolpropane, tris(hydroxyethyl)iso-cyanurate, etc.;
- tetra(allyl carbonate) of pentaerythritol;
- hexa(allyl carbonate) of dipentaerythritol;
- mixed bis(allyl carbonates) of at least two diols selected from those listed above;
- mixed poly(allyl carbonates) of at least one diol and at least one polyol selected from those specified above.

Preferred examples of poly(allyl carbonates) (A) useful for the purposes of the present invention are listed below.

- (i) bis(allyl carbonate) of diethylene glycol monomer or mixture of monomer and relative oligomers.

The bis(allyl carbonate) (i) monomer can be defined by the following general formula:



wherein R represents the radical of diethylene glycol and
n = 1.

5 The bis(allyl carbonate) (i) can be prepared by the reaction of diethylene glycol bis(chloroformate) with allyl alcohol as described, for example, in "Encyclopedia of Chemical Technology", Kirk-Othmer, III Ed., Vol. 2, pages 111-112.

10 The bis(allyl carbonate) (i), mixture of monomer (n = 1 in the above general formula) with one or more oligomers (n from 2 to about 10 in the above general formula), can be simply and conveniently prepared by means of a transesterification reaction between diallyl carbonate and diethylene glycol, operating in the presence of a
15 base catalyst as described, for example, in European patent EP 35,304. Said monomer/oligomer mixtures may generally contain up to 80% by weight of oligomers.

(ii) bis(allyl carbonate) of neopentyl glycol monomer or
20 mixture of monomer and relative oligomers.

The bis(allyl carbonate) (ii) is similar to that of (i) described above, with neopentyl glycol substituting diethylene glycol.

(iii) mixed poly(allyl carbonate) of diethylene glycol
25 and tris(hydroxyethyl) isocyanurate.

The mixed poly(allyl carbonate) (iii) can be obtained by the transesterification of diallyl carbonate with a mixture of diethylene glycol and tris(hydroxyethyl) isocyanurate as described, for example, in U.S. patent 4,812,545.

(iv) mixed poly(allyl carbonate) of neopentyl glycol and tris(hydroxyethyl) isocyanurate.

The mixed poly(allyl carbonate) (iv) is similar to that of (iii) described above, with neopentyl glycol substituting diethylene glycol.

(v) mixed poly(allyl carbonate) of 1,4-butanediol and tris(hydroxyethyl) isocyanurate.

The mixed poly(allyl carbonate) (v) is similar to that of (iii) described above, with 1,4-butanediol substituting diethylene glycol.

(vi) mixed poly(allyl carbonate) of diethylene glycol and pentaerythritol described, for example, in European patent application EP 302,537.

(vii) tris(allyl carbonate) of trimethylol propane, obtained by the reaction of diallyl carbonate with trimethylol propane under transesterification conditions.

(viii) tetrakis(allyl carbonate) of pentaerythritol, obtained by the reaction of diallyl carbonate with pentaerythritol under transesterification conditions.

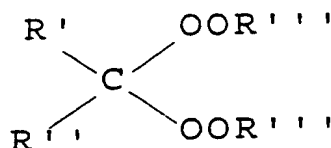
tions.

Suitable transesterification conditions are described, for example, in European patent EP 35,304 mentioned above.

5 Component (B)

Perketals which can be used as polymerization initiators for the purposes of the present invention are compounds known in the art and belonging to the group of gem-diperoxides having the following general formula:

10



wherein R''' represents a tertiary alkyl group, preferably t-butyl or t-amyl; R' and R'' each independently represent an alkyl group such as, for example, methyl, ethyl, propyl and butyl, said alkyl group optionally carrying non-interfering functional groups such as, for example, an ester alkyl group at the chain end; or R' and R'', jointly with the carbon atom to which they are bound, form a cycloalkylene group, preferably a cyclohexylidene group, said cycloalkylene group optionally substituted with one or more alkyl groups, preferably with 1-3 methyl groups.

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Specific examples of gem-diperoxides useful for the purposes of the present invention are: 2,2-di-(t-

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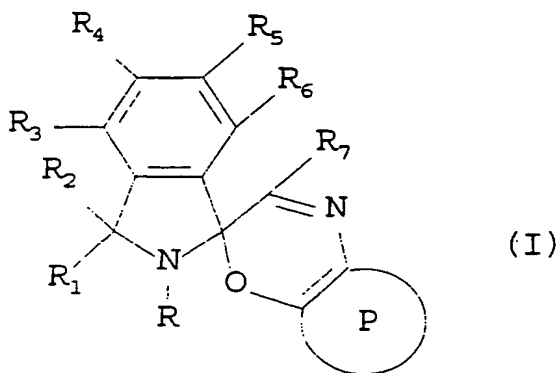
butylperoxy)butane, n-butyl-4,4-di(t-butylperoxy) valerate, ethyl-3,3-di(t-butylperoxy)valerate, 1,1-di-(t-butylperoxy)cyclohexane, 1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane, etc.

5 Cyclic gem-diperoxides and cyclic gem-triperoxides such as, for example, 3,3,6,6-tetramethyl-1,2,4,5-tetraoxane, 3,6-diethyl-3,6-dimethyl-1,2,4,5-tetraoxane, 7,8,15,16-tetraoxadispiro[5.2.5.2.]hexadecane; 3,3,6,6,-9,9-hexamethyl-1,2,4,5-tetraoxacyclononane, etc., can also be used for the purposes of the present invention.

The perketal (B) is present in the compositions object of the present invention in a quantity ranging from 0.5 to 5.0 parts, preferably from 0.8 to 2.5 parts by weight, for every 100 parts by weight of component (A).

15 Component C

Photochromatic compounds useful for the purposes of the present invention are selected from the group of spiro-isoindoline-oxazines having the following general formula (I):



25

wherein:

- R represents a linear or branched C₁-C₁₀ alkyl group, said alkyl group optionally substituted with 1-10 halogen atoms selected from fluorine, chlorine and bromine, or with C(X)₃ groups wherein X is selected from fluorine, chlorine and bromine, hydroxyl groups, linear or branched C₁-C₆ alkoxy groups, carboxyl groups, cyano groups, or with a 2,2,6,6-tetramethylpiperidine group; a vinyl group; an allyl or methallyl group; a linear or branched C₂-C₆ alkenyl group; an aryl group selected from phenyl, biphenyl and naphthyl, said aryl group optionally substituted with linear or branched C₁-C₆ alkoxy groups, carboxyl groups, amine groups, N,N-dialkyl (C₁-C₆) amine groups; a COOR' ester group wherein R' represents a linear or branched C₁-C₁₀ alkyl group; a benzyl group, said benzyl group optionally substituted with 1-5 halogen atoms selected from fluorine, chlorine and bromine, or with C(X)₃ groups wherein X is selected from fluorine, chlorine and bromine, hydroxyl groups, linear or branched C₁-C₁₀ alkyl groups, linear or branched C₁-C₆ alkoxy groups, carboxyl groups, cyano groups, or with a 2,2,6,6-tetramethylpiperidine group;
- R₁ and R₂, the same or different, represent a linear

or branched C₁-C₁₀ alkyl group, said alkyl group optionally substituted with 1-10 halogen atoms selected from fluorine, chlorine and bromine, or with C(X)₃ groups wherein X is selected from fluorine, chlorine and bromine, hydroxyl groups, linear or branched C₁-C₆ alkoxyl groups, carboxyl groups, cyano groups, or with a 2,2,6,6-tetramethylpiperidine group; a vinyl group; an allyl or methallyl group; a linear or branched C₂-C₁₀ alkenyl group; a COOR' ester group wherein R' represents a linear or branched C₁-C₁₀ alkyl group; a benzyl group, said benzyl group optionally substituted with 1-5 halogen atoms selected from fluorine, chlorine and bromine, or with C(X)₃ groups wherein X is selected from fluorine, chlorine and bromine, hydroxyl groups, linear or branched C₁-C₁₀ alkyl groups, linear or branched C₁-C₆ alkoxyl groups, carboxyl groups, cyano groups, or with a 2,2,6,6-tetramethylpiperidine group; a linear or branched C₁-C₆ alkoxyl group; an N-alkyl (C₁-C₆) amine group; an N,N-dialkyl (C₁-C₆) amine group; or, R₁ and R₂, jointly with the carbon atom to which they are bound, represent a C₄-C₁₀ cycloalkyl group, said cycloalkyl group optionally substituted with halogen atoms selected from fluorine, chlorine and bromine, or with hy-

droxyl groups, linear or branched C₁-C₆ alkoxy groups, carboxyl groups, cyano groups, amine groups, N-alkyl (C₁-C₆) amine groups, N,N-dialkyl (C₁-C₆) amine groups, N,N-dialkyl (C₁-C₆) amide groups, aryl groups selected from phenyl and biphenyl;

5

- R₃, R₄, R₅ and R₆, the same or different, represent a hydrogen atom; a halogen atom selected from fluorine, chlorine, bromine and iodine; a linear or branched C₁-C₆ alkyl group, said alkyl group optionally substituted with 1-6 halogen atoms selected

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from fluorine, chlorine and bromine, or with C(X)₃ groups wherein X is selected from fluorine, chlorine and bromine, hydroxyl groups, linear or branched C₁-C₆ alkoxy groups, carboxyl groups, cyano groups, or

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with a 2,2,6,6-tetramethylpiperidine group; a benzyl group, said benzyl group optionally substituted with 1-5 halogen atoms selected from fluorine, chlorine and bromine, or with C(X)₃ groups wherein X is selected from fluorine, chlorine and bromine, hydroxyl

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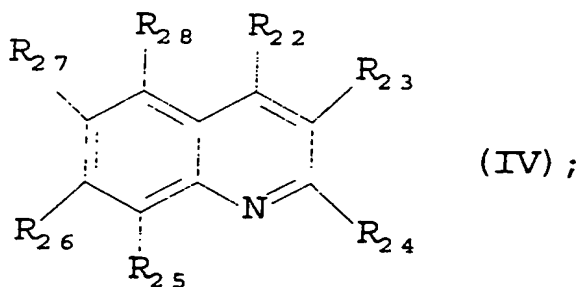
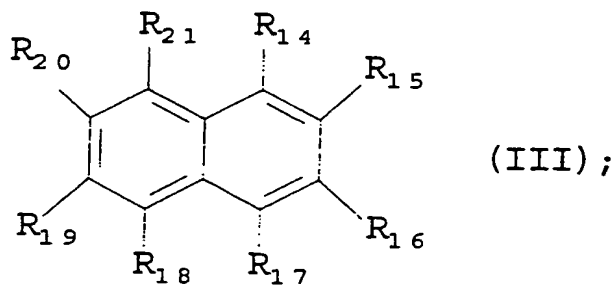
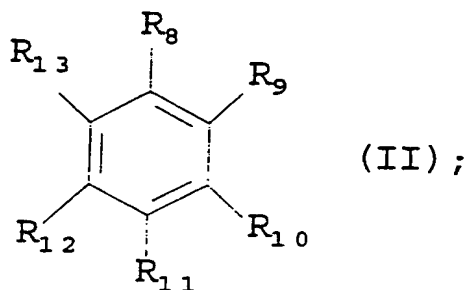
groups, linear or branched C₁-C₁₀ alkyl groups, linear or branched C₁-C₆ alkoxy groups, carboxyl groups, cyano groups, or with a 2,2,6,6-tetramethylpiperidine group; a hydroxyl group; a linear or branched C₁-C₆ alkoxy group; an amine group; an N-

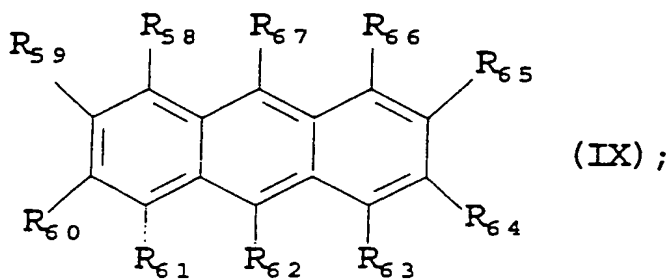
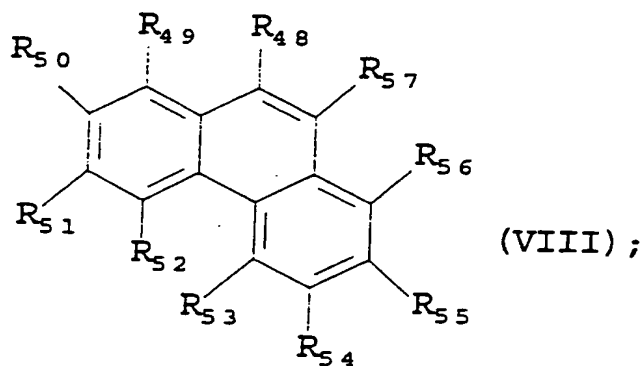
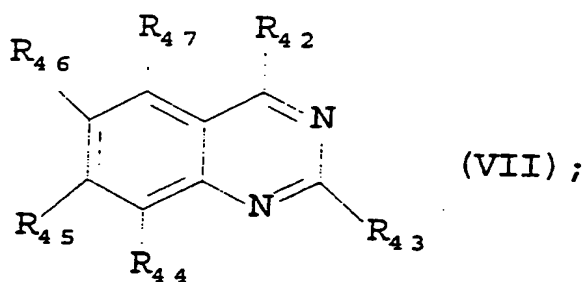
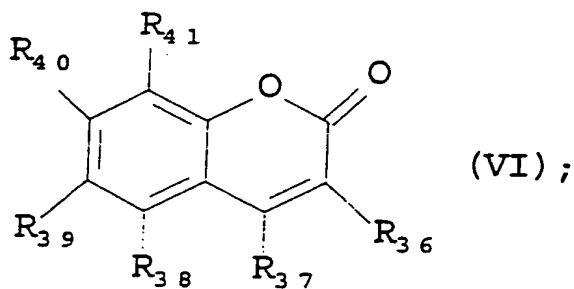
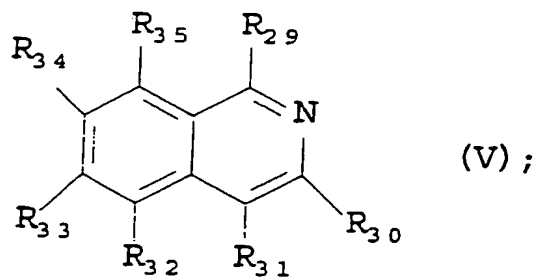
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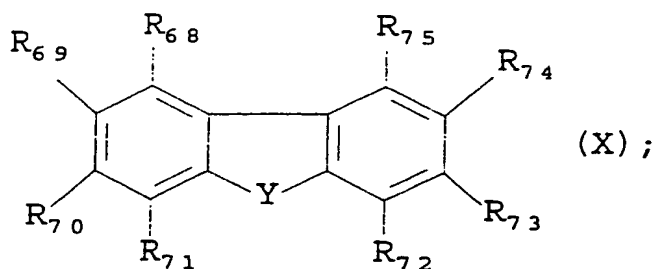
alkyl (C₁-C₆) amine group; an N,N-dialkyl (C₁-C₆)

- amine group; a piperidine, piperazine or morpholine group; a C₁-C₆ carboxyalkyl group; a C₂-C₆ carboxyalkenyl group; a carboxyamine group; N-alkyl (C₁-C₆) carboxyamine group; an N,N-dialkyl (C₁-C₆) carboxyamine group; a cyano group; a nitro group; a sulfonic group; an aryl group selected from phenyl, biphenyl and naphthyl, said aryl group optionally substituted with N,N-dialkyl (C₁-C₆) amine groups, linear or branched C₁-C₆ alkoxy groups, hydroxyl groups, linear or branched C₁-C₆ alkyl groups; an acyl group of the alkyl ketone, aryl ketone or benzyl ketone type; a linear or branched C₂-C₆ alkenyl group, said alkenyl group optionally substituted with one or two N,N-dialkyl (C₁-C₆)-4-aniline groups; an N-2,3-dihydroindoline group; a linear or branched C₁-C₆ thioether group;
- two consecutive substituents between R₃ and R₆, can represent the condensation points with other aromatic, heterocyclic or quinonic rings;
- 20 - R₇ represents a hydrogen atom; a halogen atom selected from fluorine, chlorine and bromine; a linear or branched C₁-C₆ alkyl group; a linear or branched C₁-C₆ alkoxy group; a phenyl group, a phenoxy group;
- 25 - P represents a monocyclic or polycyclic aromatic nu-

cleus, belonging to one of the following types: benzene represented by general formula (II); naphthalene represented by general formula (III); quinoline represented by general formula (IV); isoquinoline represented by general formula (V); cumarine represented by general formula (VI); quinazoline represented by general formula (VII); phenanthrene represented by general formula (VIII); anthracene represented by general formula (IX); or a heteroaromatic system represented by general formula (X):







5 wherein:

- at least two consecutive substituents between R_8 and R_{13} , R_{14} and R_{21} , R_{22} and R_{28} , R_{30} and R_{35} , R_{36} and R_{41} , R_{44} and R_{47} , R_{48} and R_{57} , R_{58} and R_{67} , R_{68} and R_{75} , represent the condensation points with the oxazine ring, the other substituents having the same meanings as substituents R_3 , R_4 , R_5 and R_6 described above;

- Y represents a CH_2 ; an oxygen atom; a nitrogen atom; a sulfur atom; or a selenium atom.

15 Preferred compounds having general formula (I) for the purposes of the present invention, are those wherein:

- R represents one of the following groups: methyl, ethyl, isopropyl, 2-allyl, 2-hydroxyethyl, 2-carboxymethyl, phenyl, 4-N,N-dimethylaminoaniline, 4-methoxybenzene, 4-cyanobenzene;
- R_1 and R_2 , the same or different, represent a methyl or phenyl group; or, considered jointly with the carbon atom to which they are bound, represent a cyclohexyl group,
- R_3 , R_4 , R_5 and R_6 , the same or different, represent a

hydrogen atom, a fluorine atom, a chlorine atom, a bromine atom, or one of the following groups: methyl, isopropyl, hydroxyl, methoxyl, N,N-dimethylamine, piperidine, morpholine, carboxyl, carboxymethyl, N,N-dimethylcarboxamide, cyano, nitro, methylketone, phenylketone, phenyl;

- R₇ represents a hydrogen atom, a chlorine atom, a bromine atom, a methyl group or a phenyl group;

- P represents one of the groups having general formula (II) to (X), wherein:

(a) two consecutive substituents between R₈ and R₁₃, R₁₄ and R₂₁, R₂₂ and R₂₈, R₃₀ and R₃₅, R₃₆ and R₄₁, R₄₄ and R₄₇, R₄₈ and R₅₇, R₅₈ and R₆₇, R₆₈ and R₇₅, represent the condensation points with the oxazine ring and the other substituents each independently represent a hydrogen atom, a fluorine atom, a chlorine atom, a bromine atom, or one of the following groups: methyl, isopropyl, hydroxyl, methoxyl, 2-hydroxyethyl, 2-allyl, piperidine, morpholine, N,N-dimethylamine, carboxyl, carboxymethyl, N,N-dimethylcarboxamide, cyano, nitro, methylketone, ethylketone, phenylketone, methylthiol;

(b) two consecutive substituents between R₈ and R₁₃, R₁₄ and R₂₁, R₂₂ and R₂₈, R₃₀ and R₃₅, R₃₆ and R₄₁,

R_{44} and R_{47} , R_{48} and R_{57} , R_{58} and R_{67} , R_{68} and R_{75} , different from those specified under point (a), represent the melting points with a benzene or quinone ring;

5 (c) Y represents an oxygen atom.

In the polymerizable liquid composition of the present invention, component (C) is used in a quantity ranging from 0.01 to 0.5 parts by weight, preferably in a quantity in the order of 0.1 parts by weight per 100
10 parts by weight of component (A).

The composition object of the present invention may optionally contain one or more conventional additives such as, for example, oxidation, light and heat stabilizers, lubricants, dyes, pigments, ultraviolet light absorbers (UV-absorbers), infra-red radiation absorbers
15 (IR-absorbers), and the like, in a total quantity however of not more than 1 part by weight for every 100 parts by weight of the compositions themselves.

Examples of additives which can be used for the purposes of the present invention are: sterically hindered
20 phenols, sterically hindered amines, benzophenones, benzotriazoles, organic phosphites and phosphonites, etc.

The composition object of the present invention containing the polymerization initiator and, optionally, one
25 or more additives selected from those mentioned above, is

transformed into the relative organic glass, operating at a temperature ranging from 30°C to 120°C, with polymerization times which generally vary from 1 hour to 100 hours.

5 The composition object of the present invention allows photochromatic organic glass with good optical characteristics to be obtained, particularly useful in the production of optical articles such as ophthalmic and safety plates and lenses; these end-products therefore
10 form an additional object of the present invention.

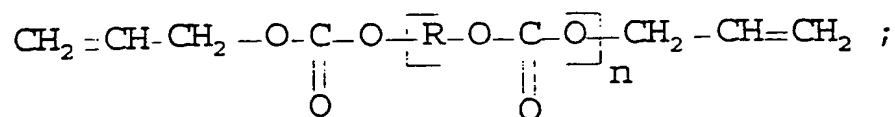
The following components were used in the following experimental examples which further illustrate the invention.

Component (A)

15 The component (A) used, hereinafter indicated as component (A₁), is the product obtained by the reaction of diallyl carbonate (DAC) with a mixture of neopentyl glycol (NPG) and tris(hydroxyethyl)isocyanurate (THEIC), in the following proportions: NPG 70% by weight; THEIC
20 30% by weight; molar ratio DAC/(NPG+THEIC) = 5/1.

The product thus obtained is a complex mixture containing:

a) bis(allyl carbonate) of neopentyl glycol, having the following general formula (monomers and oligomers):



the following composition:

monomer (n = 1) 82% by weight;

dimer (n = 2) 15% by weight;

5 trimer (n = 3) 2.4% by weight;

tetramer (n = 4) 0.4% by weight;

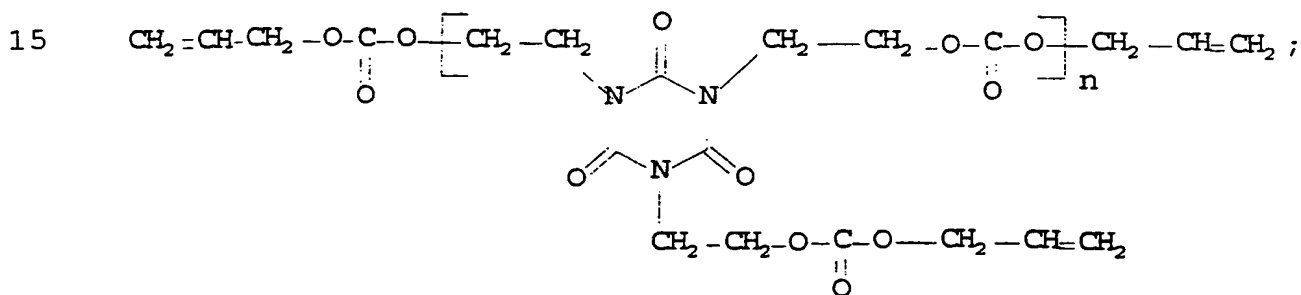
and the following physico-chemical characteristics:

- viscosity, 25°C (cst) = 53;

- density, 20°C (g/ml) = 1.096;

10 - n_D^{20} = 1.4525;

b) tris(allyl carbonate) of tris(hydroxyethyl)isocyanurate (monomer and oligomers) having the following general formula:



20

c) mixed allyl carbonates of neopentyl glycol and tris(hydroxyethyl)isocyanurate having the following physico-chemical characteristics:

- viscosity, 25°C (cst) = 80;

25 - density, 20°C (g/ml) = 1.1411;

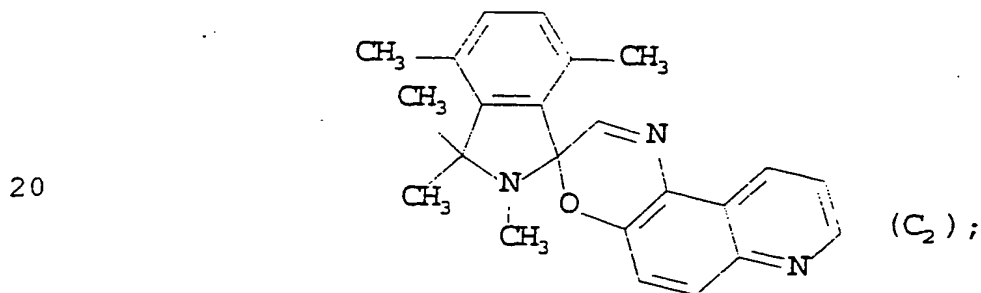
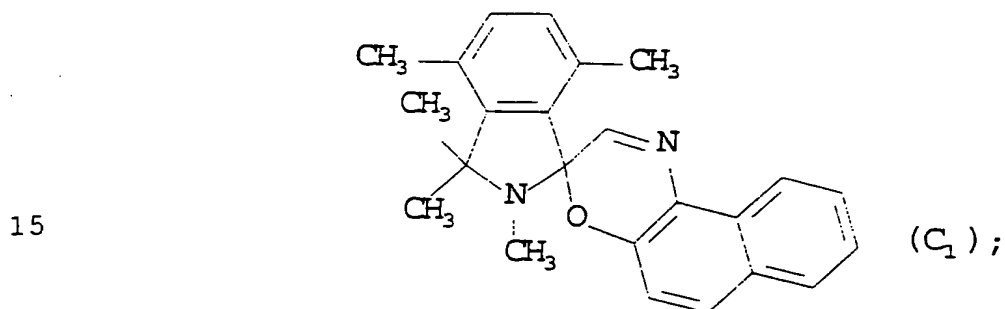
$$n_D^{20} = 1.4525;$$

Component (B)

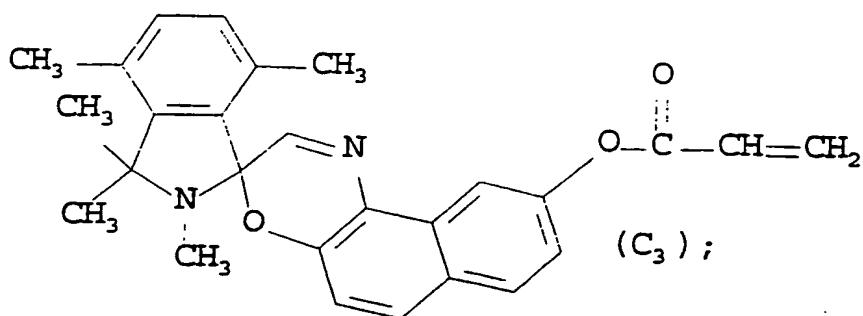
The component (B) used, hereinafter indicated as component (B₁), is 1,1-di(t-butylperoxy)-3,3,5-trimethyl-5 cyclohexane [1.5 parts by weight for every 100 parts by weight of component (A₁)].

Component (C)

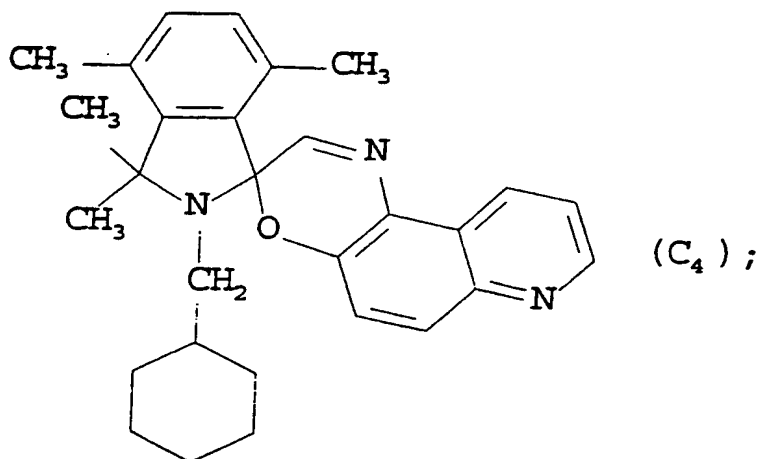
The component (C) used is selected from the following spiro-indolino-oxazines having the following formulae (C₁)-(C₅):



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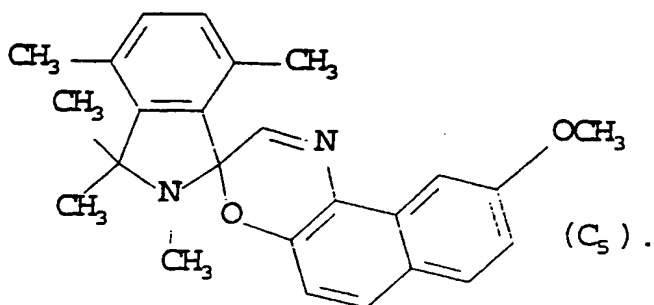


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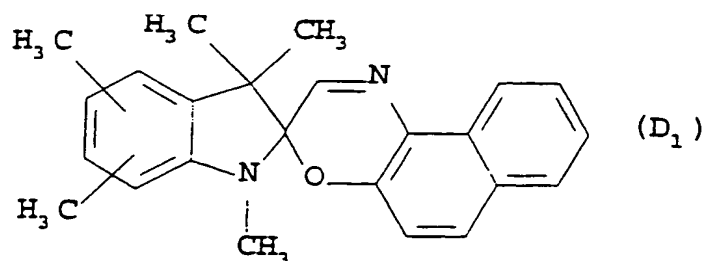


The above compounds having formula (C₁)-(C₅) are prepared as described, for example, in Italian patent application IT MI97A/01573.

The above compounds (C₁)-(C₅) are compared with two known compounds:

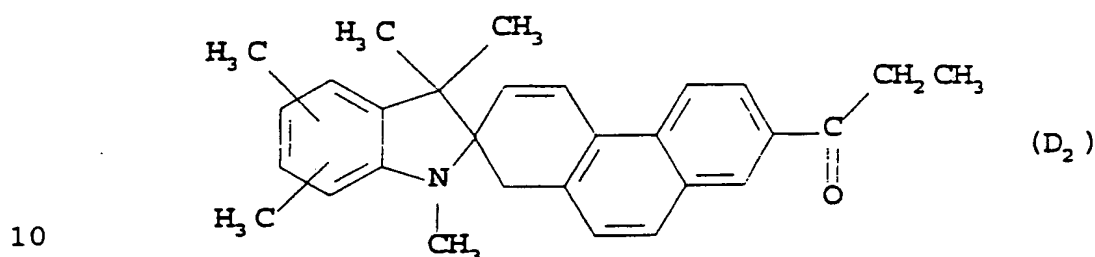
- compound (D₁) having the formula:

25



known under the trade-name of VARIACROL[®] BLUE D of
 5 Great Lakes Chemical Corporation;

- compound (D₂) having the formula:



obtained as described, for example, in European pat-
 ent application EP 432,841.

The neutral photochromatic lenses, object of the
 following experimental examples, are prepared by means of
 15 the procedure described below.

The polymerizable liquid compositions are prepared
 by mixing and homogenizing the allyl carbonate (A₁), the
 polymerization initiator (B₁) in the quantity indicated
 in the examples and, subsequently, the photochromatic
 20 compounds (C₁)-(C₅) and (D₁)-(D₂), again in the quantities
 indicated in the examples.

The compositions thus obtained are transformed, by
 means of polymerization, into neutral lenses with a
 thickness of 2 mm, by means of the conventional "casting"
 25 technique.

According to this technique, the liquid composition containing the catalyst is poured into the cavity of a mould consisting of two glass elements separated by a seal made of plasticized polyvinyl chloride (PVC) or ethylene-vinyl acetate (EVA) copolymer.

The composition is subjected to polymerization in the mould by means of the following thermal treatment, of a duration of 24 hours, in a forced air circulation oven: regulated at 70°C to 90°C in 3 hours, from 90°C to 95°C in 2 hours, isotherm at 95°C for 19 hours.

At the end of the above thermal treatment, the moulds are opened and the following characteristics are determined on the neutral photochromatic lenses thus obtained:

- (a) (λ_{\max} UVA) of the deactivated form and (λ_{\max} vis.) of the activated form;
- (b) photochromatic activity expressed as ΔY which corresponds to the difference between the Luminous Transmittance values (Y), before and after activation with a UVA lamp, radiation equal to 9 W/m², 60 seconds of radiation;
- (c) lens color in the deactivated and activated form expressed with the colorimetric values L^* , a^* and b^* (D65, 10°) as defined in Regulation CIE 1976. These values are obtained by mathematical processing of

the absorption spectrum.

The following experimental examples are provided for illustrative purposes but do not limit the scope of the present invention.

5 EXAMPLES 1-7

Compositions are prepared, containing 98.5% by weight of Component (A_1) and 1.5% by weight of component (B_1). Quantities equal to 0.1% of the total of photochromatic compounds (D_1)-(D_2) (Examples 1-2) and (C_1)-(C_3)
10 (Examples 3-7), described above, are added each time to the composition.

The liquid compositions thus obtained are subjected to polymerization according to the conditions described above. Photochromatic lenses are obtained, whose properties are indicated in Table 1, whereas Figure 1 and Figure 2 illustrate the transmittance spectra of the deactivated form of said photochromatic lenses.
15

The values of L^* , a^* and b^* indicated in Table 1 relating to lenses in the deactivated form, Figure 1 and Figure 2 clearly demonstrate how the lenses obtained using the photochromatic compounds (D_1)-(D_2) (Examples 1-2) known in the art, unlike the lenses obtained using the photochromatic compounds (C_1)-(C_3) (Examples 3-7) according to the present invention, have an intense absorption
20 between 500 nm and 580 nm corresponding to a bright pur-

ple coloring.

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Table 1

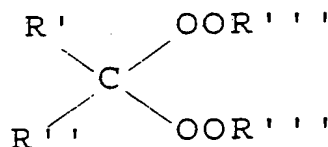
Ex.	Photochromatic compound	Deactivated lens					Activated lens					ΔY
		$\lambda_{\text{max.}}$ (UVA)	L*	a*	b*	$\lambda_{\text{max.}}$ (UVA)	L*	a*	b*			
1	(D ₁)	344	80.20	28.34	4.22	610	60.31	12.30	-24.75	28.58		
2	(D ₂)	332	77.96	23.68	-4.02	622	48.37	-9.66	-44.2	36.07		
3	(C ₁)	358	90.82	2.69	3.21	622	70.07	-13.83	-24.29	37.23		
4	(C ₂)	354	83.10	7.73	19.82	610	46.44	-10.31	-31.79	46.76		
5	(C ₃)	350	93.37	0.62	5.20	618	75.79	-13.93	-16.26	34.27		
6	(C ₄)	360	83.44	6.81	19.87	620	64.84	-12.95	-6.56	32.58		
7	(C ₅)	350	93.05	1.69	5.46	618	76.61	-8.51	-13.06	32.02		

CLAIMS

1. A liquid composition polymerizable, by means of radicalic polymerization, into photochromatic organic glass, comprising a polymerizable allyl carbonate, a polymerization initiator capable of generating free radicals under the polymerization conditions and a photochromatic compound, characterized in that:
- (A) said polymerizable allyl carbonate is at least a poly(allyl carbonate) of an aliphatic C₃-C₁₀ polyol, linear or branched, or of a cycloaliphatic C₅-C₁₆ polyol, said polyols containing from 2 to 6 hydroxyl groups in the molecule, said poly(allyl carbonates) being in the form of monomers or mixtures of monomer and relative oligomers;
- (B) said polymerization initiator, capable of generating free radicals, is at least a compound selected from the group of perketals;
- (C) said photochromatic compound is at least an organic photochromatic compound selected from the group of spiro-isoindolino-oxazines.
2. The polymerizable liquid composition according to claim 1, wherein the poly(allyl carbonates) (A) are selected from:
- bis(allyl carbonates) of diols such as, dieth-

- ylene glycol, dipropylene glycol, triethylene glycol, tetraethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 3-methyl-1,5-pentanediol, 2-methyl-2-ethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol, 1,4-dimethylolcyclohexane, 4,8-bis(hydroxymethyl[5.2.1.0^{2.6}]tricyclodecane;
- 5
- 10 - tris(allyl carbonates) of triols such as, glycerol, trimethylolpropane, tris(hydroxyethyl) isocyanurate, etc.;
- tetra(allyl carbonate) of pentaerythritol;
- hexa(allyl carbonate) of dipentaerythritol;
- 15 - mixed bis(allyl carbonates) of at least two diols selected from those listed above;
- mixed poly(allyl carbonates) of at least one diol and at least one polyol selected from those specified above.
- 20 3. The polymerizable liquid composition according to claim 2, wherein the poly(allyl carbonates) (A) are selected from:
- (i) bis(allyl carbonate) of diethylene glycol monomer or mixture of monomer and relative
- 25 oligomers.

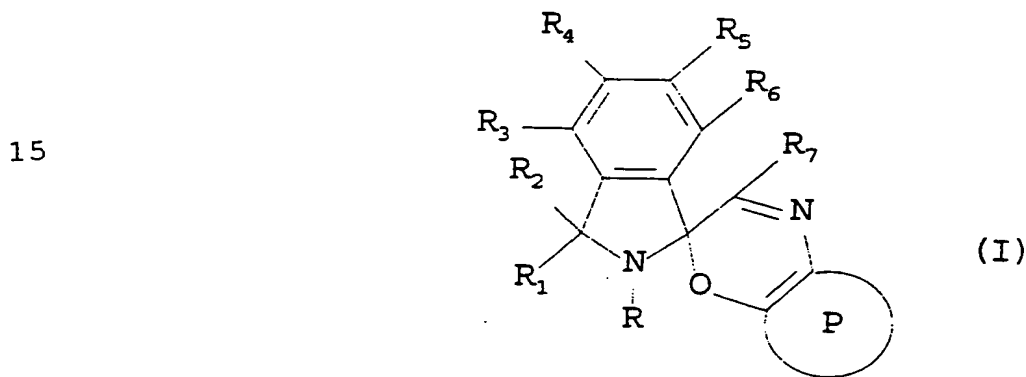
- (ii) bis(allyl carbonate) of neopentyl glycol monomer or mixture of monomer and relative oligomers.
- (iii) mixed poly(allyl carbonate) of diethylene glycol and tris(hydroxyethyl) isocyanurate.
- (iv) mixed poly(allyl carbonate) of neopentyl glycol and tris(hydroxyethyl) isocyanurate.
- (v) mixed poly(allyl carbonate) of 1,4-butanediol and tris(hydroxyethyl) isocyanurate.
- (vi) mixed poly(allyl carbonate) of diethylene glycol and pentaerythritol.
- (vii) tris(allyl carbonate) of trimethylol propane, obtained by the reaction of diallyl carbonate with trimethylol propane under transesterification conditions.
- (viii) tetrakis(allyl carbonate) of pentaerythritol, obtained by the reaction of diallyl carbonate with pentaerythritol under transesterification conditions.
4. The polymerizable liquid composition according to any of the previous claims, wherein the perketals (B) which can be used as polymerization initiators belong to the group of gem-diperoxides having the following general formula:



- wherein R''' represents a tertiary alkyl group, preferably t-butyl or t-amyl; R' and R'' each independently represent an alkyl group such as, methyl, ethyl, propyl and butyl, said alkyl group optionally carrying non-interfering functional groups such as, an ester alkyl group at the chain end; or R' and R'', jointly with the carbon atom to which they are bound, form a cycloalkylene group, said cycloalkylene group optionally substituted with one or more alkyl groups, preferably with 1-3 methyl groups.
5. The polymerizable liquid composition according to claim 4, wherein the perketals (B) are: 2,2-di-(t-butylperoxy)butane, n-butyl-4,4-di(t-butylperoxy)valerate, ethyl-3,3-di(t-butylperoxy)valerate, 1,1-di-(t-butylperoxy)cyclohexane, 1,1-di(t-butylperoxy)3,3,5-trimethylcyclohexane.
 6. The polymerizable liquid composition according to claim 1, wherein the perketals (B) are selected from cyclic gem-peroxides and cyclic gem-triperoxides.
 7. The polymerizable liquid composition according to claim 6, wherein the perketals (B) are: 3,3,6,6-tetramethyl-1,2,4,5-tetraoxane, 3,6-diethyl-3,6-dimethyl-1,2,4,5-tetraoxane, 7,8,15,16-tetraoxadispi-

ro[5.2.5.2.]hexadecane; 3,3,6,6,-9,9-hexamethyl-
1,2,4,5-tetraoxacyclononane.

8. The polymerizable liquid composition according to
any of the previous claims, wherein the perketal (B)
5 is present in a quantity ranging from 0.5 to 5.0
parts for every 100 parts by weight of component
(A).
9. The polymerizable liquid composition according to
any of the previous claims, wherein the photochro-
10 matic compounds (C) are selected from the group of
spiro-indoline-oxazines having the following gen-
eral formula (I):



wherein:

- 20 - R represents a linear or branched C₁-C₁₀ alkyl
group, said alkyl group optionally substituted
with 1-10 halogen atoms selected from fluorine,
chlorine and bromine, or with C(X)₃ groups
wherein X is selected from fluorine, chlorine
25 and bromine, hydroxyl groups, linear or

5 branched C₁-C₆ alkoxy groups, carboxyl groups,
cyano groups, or with a 2,2,6,6-tetramethylpiperidine group; a vinyl group; an
allyl or methallyl group; a linear or branched
10 C₂-C₆ alkenyl group; an aryl group selected
from phenyl, biphenyl and naphthyl, said aryl
group optionally substituted with linear or
branched C₁-C₆ alkoxy groups, carboxyl groups,
amine groups, N,N-dialkyl (C₁-C₅) amine groups;
15 a COOR' ester group wherein R' represents a
linear or branched C₁-C₁₀ alkyl group; a benzyl
group, said benzyl group optionally substituted
with 1-5 halogen atoms selected from fluorine,
chlorine and bromine, or with C(X)₃ groups
20 wherein X is selected from fluorine, chlorine
and bromine, hydroxyl groups, linear or
branched C₁-C₁₀ alkyl groups, linear or branched
C₁-C₆ alkoxy groups, carboxyl groups, cyano
groups, or with a 2,2,6,6-tetramethylpiperidine
group;

25 R₁ and R₂, the same or different, represent a linear
or branched C₁-C₁₀ alkyl group, said alkyl group op-
tionally substituted with 1-10 halogen atoms se-
lected from fluorine, chlorine and bromine, or with
C(X)₃ groups wherein X is selected from fluorine,

chlorine and bromine, hydroxyl groups, linear or
branched C₁-C₆ alkoxyl groups, carboxyl groups,
cyano groups, or with a 2,2,6,6-tetramethyl-
piperidine group; a vinyl group; an allyl or methal-
5 lyl group; a linear or branched C₂-C₁₀ alkenyl group;
a COOR' ester group wherein R' represents a linear
or branched C₁-C₁₀ alkyl group; a benzyl group, said
benzyl group optionally substituted with 1-5 halogen
atoms selected from fluorine, chlorine and bromine,
10 or with C(X)₃ groups wherein X is selected from
fluorine, chlorine and bromine, hydroxyl groups,
linear or branched C₁-C₁₀ alkyl groups, linear or
branched C₁-C₆ alkoxyl groups, carboxyl groups,
cyano groups, or with a 2,2,6,6-tetramethyl-
15 piperidine group; a linear or branched C₁-C₆ alkoxyl
group; an N-alkyl (C₁-C₆) amine group; an N,N-
dialkyl (C₁-C₆) amine group; or, R₁ and R₂, consid-
ered jointly with the carbon atom to which they are
bound, represent a C₄-C₁₀ cycloalkyl group, said cy-
20 cloalkyl group optionally substituted with halogen
atoms selected from fluorine, chlorine and bromine,
or with hydroxyl groups, linear or branched C₁-C₆
alkoxyl groups, carboxyl groups, cyano groups, amine
groups, N-alkyl (C₁-C₆) amine groups, N,N-dialkyl
25 (C₁-C₆) amine groups, N,N-dialkyl (C₁-C₆) amide

groups, aryl groups selected from phenyl and biphenyl;

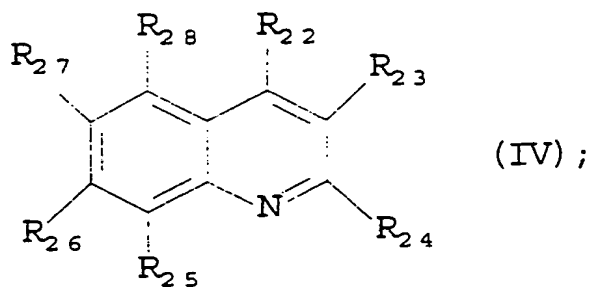
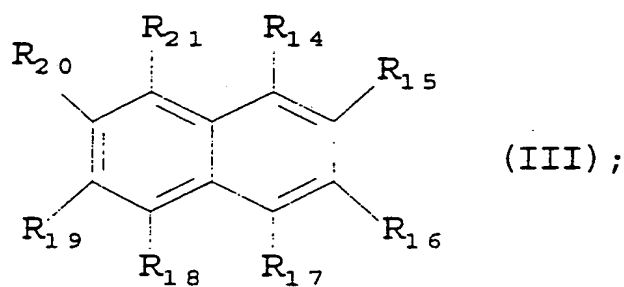
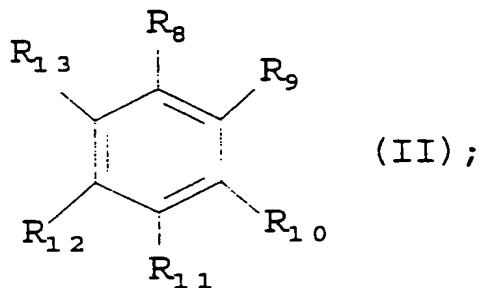
- 5 - R_3 , R_4 , R_5 and R_6 , the same or different, represent a hydrogen atom; a halogen atom selected from fluorine, chlorine, bromine and iodine; a linear or branched C_1 - C_6 alkyl group, said alkyl group optionally substituted with 1-6 halogen atoms selected from fluorine, chlorine and bromine, or with $C(X)_3$ groups wherein X is selected from fluorine, chlorine and bromine, hydroxyl groups, linear or branched C_1 - C_6 alkoxy groups, carboxyl groups, cyano groups, or with a 2,2,6,6-tetramethylpiperidine group; a benzyl group, said benzyl group optionally substituted with 1-5 halogen atoms selected from fluorine, chlorine and bromine, or with $C(X)_3$ groups wherein X is selected from fluorine, chlorine and bromine, hydroxyl groups, linear or branched C_1 - C_{10} alkyl groups, linear or branched C_1 - C_6 alkoxy groups, carboxyl groups, cyano groups, or with a 2,2,6,6-tetramethylpiperidine group; a hydroxyl group; a linear or branched C_1 - C_6 alkoxy group; an amine group; an N-alkyl (C_1 - C_6) amine group; an N,N-dialkyl (C_1 - C_6) amine group; a piperidine, piperazine or mor-
- 10
- 15
- 20
- 25

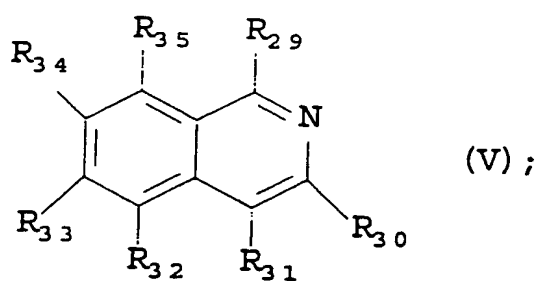
pholine group; a C₁-C₆ carboxyalkyl group; a C₂-C₆ carboxyalkenyl group; a carboxyamine group; N-alkyl (C₁-C₆) carboxyamine group; an N,N-dialkyl (C₁-C₆) carboxyamine group; a cyano group; a nitro group; a sulfonic group; an aryl group selected from phenyl, biphenyl and naphthyl, said aryl group optionally substituted with N,N-dialkyl (C₁-C₆) amine groups, linear or branched C₁-C₆ alkoxy groups, hydroxyl groups, linear or branched C₁-C₆ alkyl groups; an acyl group of the alkyl ketone, aryl ketone or benzyl ketone type; a linear or branched C₂-C₆ alkenyl group, said alkenyl group optionally substituted with one or two N,N-dialkyl (C₁-C₆)-4-aniline groups; an N-2,3-dihydroindoline group; a linear or branched C₁-C₆ thioether group;

- two consecutive substituents between R₃ and R₆, can represent the condensation points with other aromatic, heterocyclic or quinonic rings;

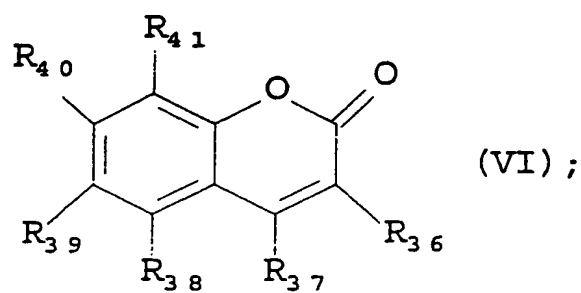
- R₇ represents a hydrogen atom; a halogen atom selected from fluorine, chlorine and bromine; a linear or branched C₁-C₆ alkyl group; a linear or branched C₁-C₆ alkoxy group; a phenyl group, a phenoxyl group;

- P represents a monocyclic or polycyclic aromatic nucleus, belonging to one of the following types: benzene represented by general formula (II); naphthalene represented by general formula (III); quinoline represented by general formula (IV); isoquinoline represented by general formula (V); coumarin represented by general formula (VI); quinazoline represented by general formula (VII); phenanthrene represented by general formula (VIII); anthracene represented by general formula (IX); or a heteroaromatic system represented by general formula (X):

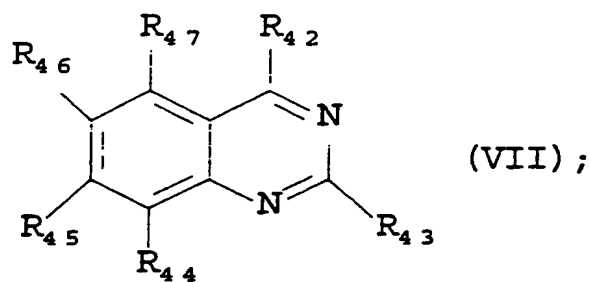




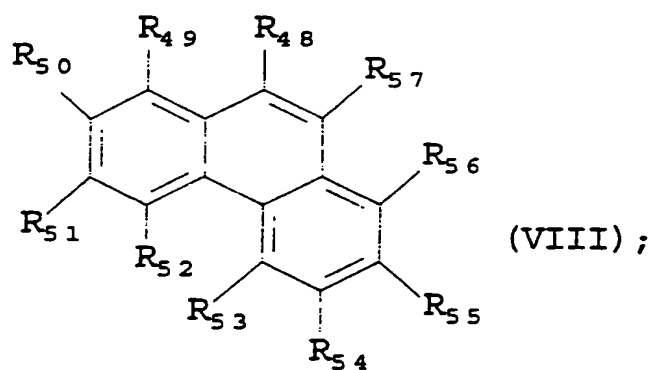
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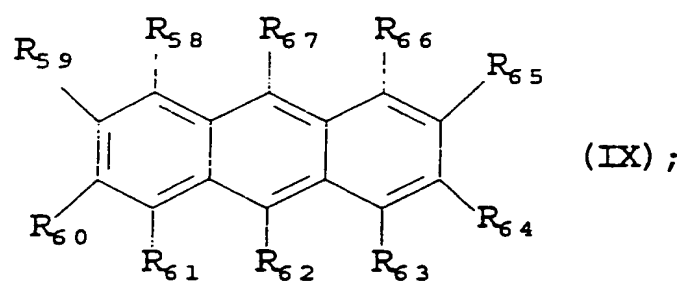
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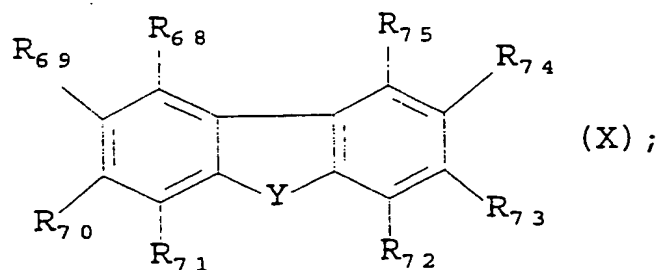
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wherein:

- at least two consecutive substituents between
 10 R_8 and R_{13} , R_{14} and R_{21} , R_{22} and R_{27} , R_{30} and R_{35} ,
 R_{36} and R_{41} , R_{44} and R_{47} , R_{48} and R_{57} , R_{58} and R_{67} ,
 R_{68} and R_{75} , represent the condensation points
 with the oxazine ring, the other substituents
 having the same meanings as substituents R_3 ,
 15 R_4 , R_5 and R_6 described above;
- Y represents a CH_2 ; an oxygen atom; a nitrogen
 atom; a sulfur atom; or a selenium atom.

10. The polymerizable liquid composition according to
 claim 9, wherein the compounds having general for-
 mula (I) are those wherein:
 20

- R represents one of the following groups:
 methyl, ethyl, isopropyl, 2-allyl, 2-hydro-
 xyethyl, 2-carboxymethyl, phenyl, 4-N,N-
 dimethylaminoaniline, 4-methoxybenzene, 4-cya-
 25 nobenzene;

- R_1 and R_2 , the same or different, represent a methyl or phenyl group; or, considered jointly with the carbon atom to which they are bound, represent a cyclohexyl group,
- 5 - R_3 , R_4 , R_5 and R_6 , the same or different, represent a hydrogen atom, a fluorine atom, a chlorine atom, a bromine atom, or one of the following groups: methyl, isopropyl, hydroxyl, methoxyl, N,N-dimethylamine, piperidine, morpholine, carboxyl, carboxymethyl, N,N-dimethyl-
10 carboxamide, cyano, nitro, methylketone, phenylketone, phenyl;
- R_7 represents a hydrogen atom, a chlorine atom, a bromine atom, a methyl group or a phenyl
15 group;
- P represents one of the groups having general formula (II) to (X), wherein:
 - (a) two consecutive substituents between R_8 and R_{13} , R_{14} and R_{21} , R_{22} and R_{28} , R_{30} and R_{35} , R_{36} and R_{41} , R_{44} and R_{47} , R_{48} and R_{57} , R_{58} and R_{67} , R_{68} and R_{75} , represent the condensation points with the oxazine ring and the other substituents each independently represent a hydrogen atom, a fluorine
20 atom, a chlorine atom, a bromine atom, or
25 atom, a chlorine atom, a bromine atom, or

one of the following groups: methyl, isopropyl, hydroxyl, methoxyl, 2-hydroxyethyl, 2-allyl, piperidine, morpholine, N,N-dimethylamine, carboxyl, carboxymethyl, N,N-dimethyl-carboxamide, cyano, nitro, methylketone, ethylketone, phenyl-ketone, methylthiol;

(b) two consecutive substituents between R_2 and R_{13} , R_{14} and R_{21} , R_{22} and R_{28} , R_{30} and R_{35} , R_{36} and R_{41} , R_{44} and R_{47} , R_{48} and R_{57} , R_{58} and R_{67} , R_{68} and R_{75} , different from those specified under point (a), represent the melting points with a benzene or quinone ring;

(c) Y represents an oxygen atom.

11. The polymerizable liquid composition according to any of the previous claims, wherein component (C) is used in a quantity ranging from 0.01 to 0.5 parts by weight per 100 parts by weight of component (A).

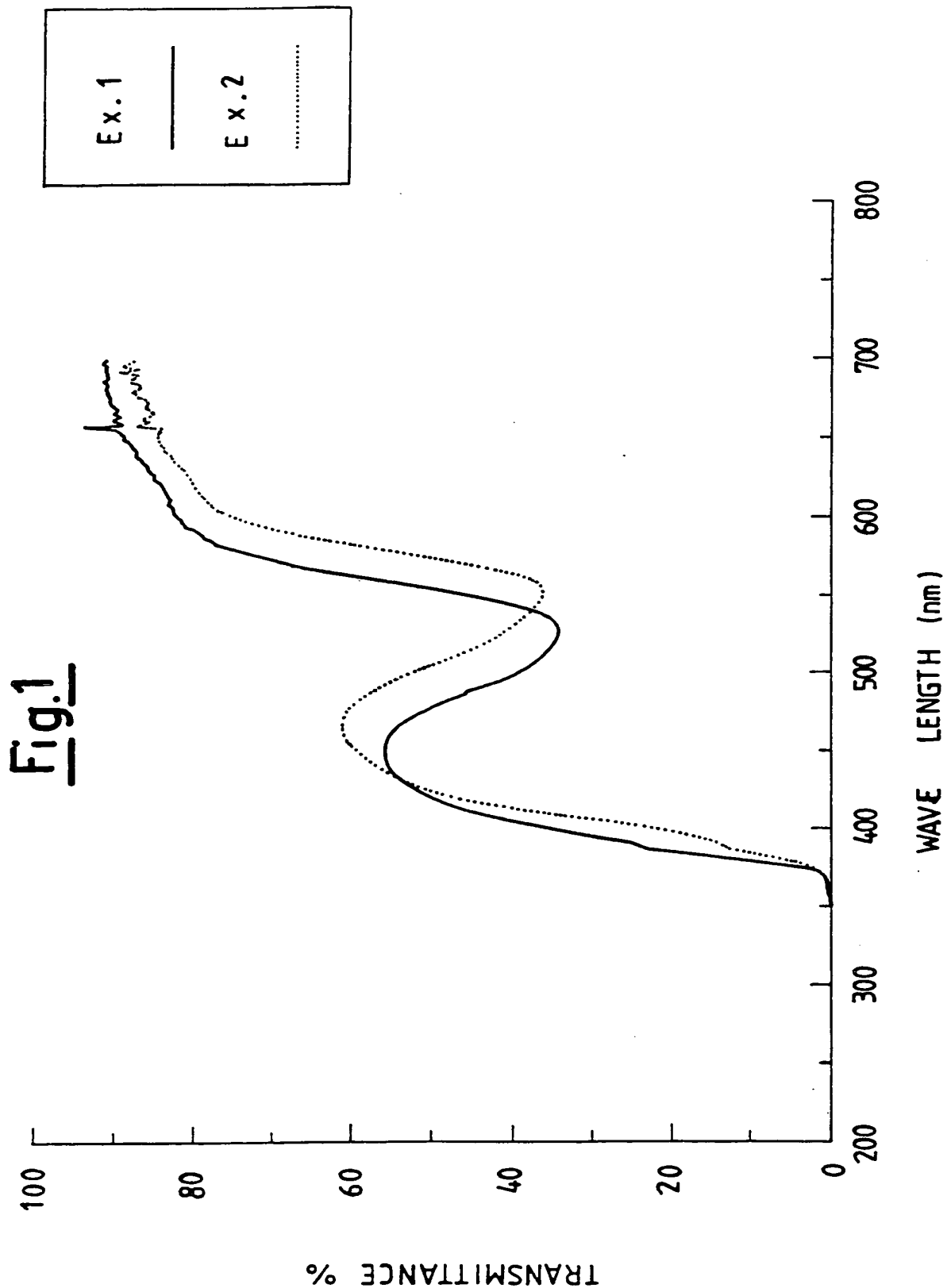
12. The polymerizable liquid composition according to any of the previous claims, containing one or more conventional additives such as, for example, oxidation, light and heat stabilizers, lubricants, dyes, pigments, ultraviolet light absorbers (UV-absorbers), infra-red radiation absorbers (IR-

absorbers), and the like, in a total quantity however of not more than 1 part by weight for every 100 parts by weight of the compositions themselves.

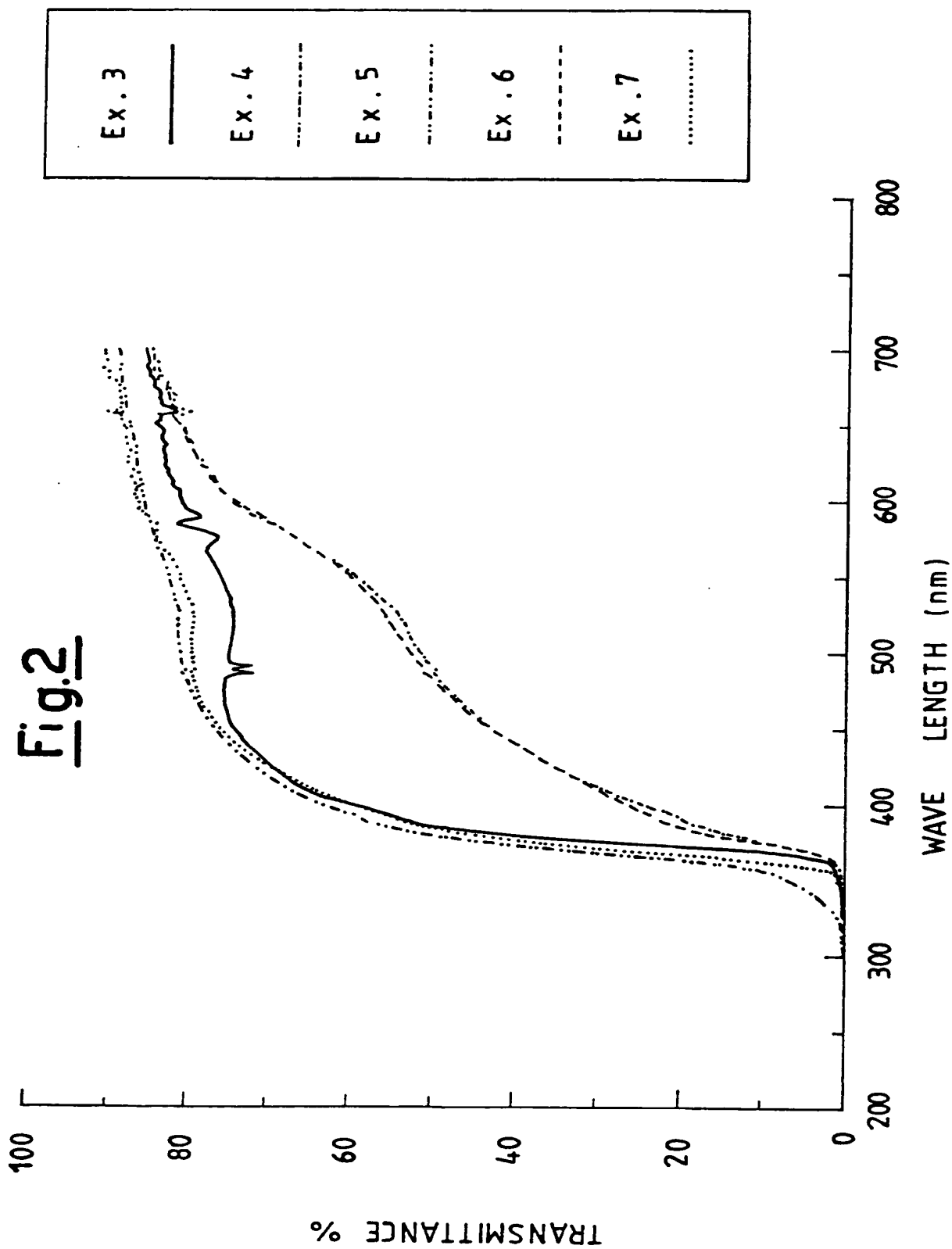
13. Photochromatic organic glass obtained by the polymerization of the liquid composition according to any
5 of the previous claims.
14. Optical articles, such as safety and ophthalmic plates and lenses obtained from the organic glass according to claim 13.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/08872

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F18/24 C08F2/44 C08K5/357 C08L69/00 G02B1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F C08K G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 595 424 A (ENICHEM SINTESI) 4 May 1994 (1994-05-04) page 10 -page 11; examples ---	1-5, 9, 12-14
A	WO 95 04086 A (EFFER ERHARD ;MELZIG MANFRED (DE); ZINNER HERBERT (DE); RODENSTOCK) 9 February 1995 (1995-02-09) page 8; claims 1,3 ---	1-3, 9, 12-14
A	GB 1 561 079 A (AMERICAN OPTICAL CORP) 13 February 1980 (1980-02-13) examples 9,10 ---	1-3, 12-14
A	EP 0 227 337 A (PILKINGTON BROTHERS PLC) 1 July 1987 (1987-07-01) page 4, line 14 - line 16; examples --- -/--	1-14

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

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L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

6 February 2001

Date of mailing of the international search report

26/02/2001

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INTERNATIONAL SEARCH REPORT

Inte. onal Application No

PCT/EP 00/08872

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International Application No

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